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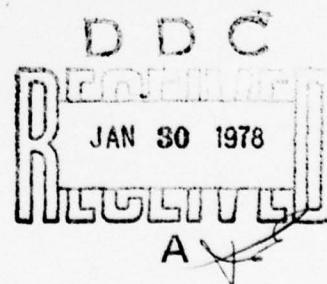# EFFECT OF MOLECULAR ROTATION ON VIBRATIONAL RELAXATION

Optical Sciences Center
University of Arizona
Tucson, AZ 87521   402821

August 1977

Final Report

Approved for public release; distribution unlimited

AIR FORCE WEAPONS LABORATORY
Air Force Systems Command
Kirtland Air Force Base, NM 87117

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This final report for Contract F29601-74-A-0023-0001 studies the effect of molecular rotation on vibrational relaxation. A model for complicated vibrational collisions is developed. Changes in the molecular rotation are of significant importance in vibration collision processes and dominate deactivation processes at thermal velocities.

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PORT STUDIES THE EFFECT OF MOLECULAR ROTATION ON VIBRATIONAL RELAXATION.
OMPLICATED VIBRATIONAL COLLISIONS IS DEVELOPED. CHANGES IN THE
ATION ARE OF SIGNIFICANT IMPORTANCE IN VIBRATION COLLISION PROCESSES AND
TIVATION PROCESSES AT THERMAL VELOCITIES.

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SECTION I

INTRODUCTION

The purpose of this contract is to develop a theory that
describes the vibrational-vibrational collision processes within the
bending mode of CO_2 and the cross collisions between the bending mode
and the symmetric stretch mode. These processes play a vital role in
the deactivation of the lower state of the CO_2 laser transition. The
technical problems associated with the problem are simply stated. First,
CO_2 is a linear triatomic molecule, and it is unclear whether existent
theories, which are restricted to diatomic systems, will work. Second,
since CO_2 is linear, the bending mode is degenerate, which leads to an
ambiguity between vibrational and rotational motion (called "vibrational
angular momentum"), which gives rise to a doubling of the bending mode.
Because of the uncertainty with how to proceed, a Born theory is used,
which is relatively simple conceptually and which can, in principle,
lead to the information needed to rationally attack the problem.

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SECTION II

TECHNIQUE

In this section, a simple technique is presented for calculating

the matrix elements of the intermolecular potential between colliding

molecules undergoing vibrational energy transfer or conversion pro-

cesses. The theory of vibrational relaxation processes in diatomic

or polyatomic molecular gases (Refs. 1 and 2) depends critically on

these matrix elements. To date, most calculations of (molecular)

inelastic collision cross sections have employed a set of questionable

approximations in computing the relevant matrix elements (Refs. 3

through 5). While these approximations greatly simplify the calcula-

tions, they lack sound justification and in some cases are not valid.

For collisions between two molecular systems, most calculations consider

only (1) collinear collisions and (2) interactions between nearest

neighbors. In addition, the colliding potential is approximated by

a simple repulsive exponential.

The first two approximations are kinematic, and their effect is

to eliminate all of the angular factors that would otherwise arise in

the collision process. To simulate the full set of possible initial

collision orientations, a steric factor $P_0 = 1/3$ for each molecule is

introduced into the transition amplitude. The second approximation

is justified on the grounds that it is the short-range portion of the

collision potential that dominates the dynamics of vibrational transfer

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and conversion processes. Unfortunately, the steric factor tends to
vary with the colliding molecular species, and there does not exist a
reliable quantitative theory for calculating this factor for collisions
involving nonlinear polyatomic molecules (Ref. 6). The second approxi-
mation is clearly invalid for initial collision orientations in which
one atom of one molecule is very close to a number of atoms in the
second molecule. Furthermore, one cannot investigate the possibility
of rotational transfer or conversion occurring simultaneously with
vibrational processes. Finally, with regard to these kinematic approxi-
mations, it should be noted that Mies (Ref. 7) has carried out a
first-principle's calculation using the full-angle-dependent potential
for the excitation of hydrogen molecules by helium atoms. His results
have raised grave doubts about the validity of items (1) and (2) above.

Assume that the potential can be approximated by

$$U = \sum_{i,j} U_{i,j} (\vec{r} - \vec{R}_i^{(a)} + \vec{R}_j^{(b)}) \tag{1}$$

Here, $U_{i,j}$ is the interaction between atom i in polyatomic molecule A
and atom j in polyatomic molecule B, $\vec{r}$ is the vector between the molecular
center of masses, and $\vec{R}_i^{(a)} \vec{R}_j^{(b)}$ is the position vector of atom $i(j)$
from the center of mass of molecule $A(B)$. Equation (1) assumes that
the electronic degrees of freedom are not excited by the collision and
in addition, that $\vec{s} = \vec{r} - \vec{R}_i^{(a)} + \vec{R}_j^{(b)}$ is the only vector direction
that is significant. Thus, one neglects (orientational) dipole-dipole
forces, etc., which are believed to dominate only the long-range portion
of the intermolecular potential (Ref. 8). This part of the intermolecular

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force gives rise only to rotational processes and plays no role in vibrational relaxation.

For situations in which the Born approximation applies, the matrix elements of equation (2) are required between the states $|\vec{k};\alpha,\beta\rangle$ and $|\vec{k}';\alpha',\beta'\rangle$. Here $\vec{k}(\vec{k}')$ is the relative center-of-mass wave vector before (after) the collision, $\alpha(\alpha')$ is the initial (final) rotation-vibration state of molecule A, and $\beta(\beta')$ is the same, but for molecule B. The relevant matrix element is then

$$\langle\vec{k}';\alpha',\beta'|U|\vec{k};\alpha,\beta\rangle \;=\; \sum_{i,j} U_{i,j}(\vec{q})F^{i}_{\alpha\to\alpha'}(-\vec{q})F^{j}_{\beta\to\beta'}(\vec{q}) \tag{2}$$

where $\hbar\vec{q}$ is the momentum transfer vector and $F^{i}_{\alpha\to\alpha'}(-\vec{q}) = \langle\alpha'|\exp(-i\vec{q}\cdot\vec{R}_{i}^{(a)}|\alpha\rangle$ is the form factor of atom i between molecular states $|\alpha\rangle$ and $|\alpha'\rangle$ at wave vector $\vec{q}$. These quantities, which also appear in neutron scattering, depend only on the molecular structure, the initial and final rotation-vibration states, and the wave vector $\vec{q}$. They are independent of the colliding potential and for some transitions may be obtainable from neutron scattering experiments (Ref. 9). The factors $U_{i,j}(\vec{q})$ are the Fourier transform of the atom-atom interaction. This approach separates the internal dynamics of the molecule (i.e., the form factors $F^{i}_{\alpha\to\alpha'}(-\vec{q})$) from the center-of-mass motion (i.e., the $U_{i,j}(\vec{q})$) and is formally similar to the approach taken for inelastic collisions between fast electrons and atoms (Ref. 10). Finally, it should be noted that all of the approximations mentioned above have been avoided.

For most molecular systems one cannot use the Born approximation for collisions occurring at thermal velocities and one must resort to

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other techniques. One approach is the Born approximation to the reactance matrix. This technique was used by Burke and Seaton (Ref. 11) to study e-H collision cross sections. Their efforts were successful and can be adapted readily to our problem.

In general, one expects that many partial waves will be required to adequately describe the cross section for inelastic processes. Consequently, one should avoid a partial wave analysis and use the expression

$$\langle \vec{k}', \alpha', \beta' | t | \vec{k}, \alpha, \beta \rangle = \frac{-2i(2mk/\hbar^2)\langle \vec{k}', \alpha', \beta' | U | \vec{k}, \alpha, \beta \rangle}{1 - i(2mk/\hbar^2)\langle k', \alpha', \beta' | U | \vec{k}, \alpha, \beta \rangle} \tag{3}$$

for the transmission matrix.

SECTION III

DISCUSSION

As discussed in Section II, the collision matrix elements decompose into individual atom-atom contributions times a term describing the center-of-mass motion. This leads to a model of collisions that is called the "form factors" model following the usage of this model in nuclear theory. The basic idea is to regard each pair of components (e.g., O and C) to be the same independent of the molecule in which it is situated. In practice, the atmosphere has only four interesting atoms (H, O, C, and N) and the CO_2 laser only one more (He); thus, one can describe all collisions of interest with a relatively limited number of parameters. In the case of the collision of CO_2 molecules, there are only three collision potentials (O-O, O-C, C-C) that can be determined by comparison with the collisions of CO with itself--a problem that is fairly well developed both theoretically and experimentally.

In the specific approach, a relatively simple problem was chosen, the collision of He with N_2, because of its significance to the CO_2 laser problem and because it involves one of the simplest of the homonuclear diatomics. Furthermore, it is somewhat analogous to collisions involving hydrogen, which is a system about which a great deal is known. This work was initially developed into a short paper whose material is included in this report. Several purposes were served in the study. It showed that the results of the calculation were

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sensible and that calculations were possible. More subtly it demonstrated
that quantum mechanical effects were important.

The investigation given in the paper involved relative cross sections,
which are used to determine the range but not the magnitude of the
potential. For that, one must be able to calculate the absolute
cross sections. To do this, it is necessary to unitarize the calculation,
i.e., to correct for the fact that probability conservation is violated
in the Born approximation. Many unitarization schemes exist and are
tested for collisions with hydrogen. The scheme outlined in Section II
was tried and proved to be successful for e^- and He collisions. How-
ever, an unresolved difficulty was encountered. The unitarization pro-
cedure involves the computation of all nonunitarized cross sections
before the unitarized values can be found. As is seen in Section IV,
there are significant contributions from large values of angular momentum
transfer ($\Delta J = 12$) and therefore intricate dependences on the m values
(i.e., angular dependences). These numerical problems become worse as
J increases, and there are enormous problems in finding an appropriate
cutoff point. At the end of the contract year, this problem had not
been solved. However, unitarization may not be as important as first
believed, and the difficulties may not be fatal to the scheme.

SECTION IV

CALCULATIONS

In this section, the method described above is applied to calculate
the scattering cross sections for vibrational, rotational, translational
collision rates between He and N_2. In particular, excitation from the
vibrational ground state ($\nu = 0$) to the $\nu = 1$ state is considered and the
following three features are examined: (1) The effect of the initial
rotational state, (2) the importance of angular momentum transfer during
a vibrational encounter, and (3) the effects of molecular orientation
(i.e., the M_J quantum number) in these collisions.

For the purposes of illustration, the inelastic scattering of He
with N_2 is treated within the first Born approximation. As inelastic
vibrational processes generally involve the short-range portion of the
collision potential, which is quite large, the first Born approximation
will not yield collision cross sections whose absolute magnitudes are
reliable. However, it does yield accurate results for the relative
sizes of such cross sections for different inelastic processes. For
example, in charge transfer collisions between alpha particles and
hydrogen, the ratios of the inelastic cross sections to different final
states remain unchanged in going from the Born approximation to much
more sophisticated approaches although the magnitude of the various
cross sections varies by several factors of 10 (Refs. 12 and 13).
Furthermore, experimental results for these ratios are within 10%

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agreement with those predicted by the Born approximation.*

For our present purposes, these ratios are sufficient, and our results are qualitatively reliable.

Using the techniques described in Section II, it can be assumed for the purposes of vibrational collisions that the short-range piece of the He-N_2 interaction can be written as

$$U(\vec{r};\vec{R}_1,\vec{R}_2) \;=\; U_1(\vec{r} - \vec{R}_1) + U_2(\vec{r} - \vec{R}_2) \tag{4}$$

where $\vec{r}$ is the vector distance between the He atom and the center of mass of the N_2 molecule. The vectors $\vec{R}_1$ and $\vec{R}_2$ locate the position of the nitrogen atom in question relative to the molecular center of mass. The quantity $U_1(\vec{r} - \vec{R}_1)[U_2(\vec{r} - \vec{R}_2)]$ is the interaction potential between atom 1[2] and the He atom. For homonuclear diatomic molecules $U_1 = U_2$, and for simplicity a Yukawa type interaction with a range of 0.1 nm has been assumed.

Within the first Born approximation, the inelastic scattering cross section between the (initial) molecular state $|vJM_J\rangle$ and the (final) molecular state $|v'J'M_J'\rangle$ is (the He atom is assumed to remain in its ground state)

$$\sigma_{vJM_J \to v'J'M_J'}(k_i) \;=\; \left(\frac{\mu}{2\pi\hbar^2 k_i}\right)^2 \int d\vec{g}\, U_1{}^2(\vec{g}) \,|\mathcal{F}_{vJM_J \to v'J'M_J'}(\vec{g})|^2 \tag{5}$$

where μ is the reduced mass of the He-N_2 system, and $U_1(\vec{g})$ is the Fourier transform of the Yukawa potential. For a homonuclear diatomic molecule such as N_2, the form factor $\mathcal{F}_{vJM_J \to v'J'M_J'}(\vec{g})$ is given by

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*Yale data, unpublished.

$$\mathcal{F}_{\nu J M_J \to \nu' J' M_J'}(\vec{g}) = 2\langle\nu'J'M_J'|\cos(\tfrac{1}{2}\vec{g}\cdot\vec{R})|\nu J M_J\rangle \tag{6}$$

where $\vec{R}$ is the instantaneous vector distance between the two nitrogen atoms (in the N_2 molecule). If the axis of quantization is taken parallel to the momentum transfer vector $(\vec{g})$, then the selection rule $M_J = M_J'$ follows. A similar situation arises in neutron scattering (Ref. 9). Finally, note that symmetry demands that both J and J' be even.

SECTION V

RESULTS

For convenience, this discussion is confined to vibrational excitation (de-excitation) from the ground (first-excited) to the first-excited (ground) vibrational state. In problems involving atmospheric propagation or in typical laser systems one generally finds that a large number of different rotational states are occupied. This is especially true for molecules such as CO_2 or N_2. Consequently, one must investigate the effect of the initial angular momentum state on the collision process. One can readily convince oneself that the best measure of this feature is to examine $V \rightarrow T$ collision process, i.e., inelastic events in which $\Delta J = 0$ (but with $\Delta \nu = 1$, of course). In Figure 1 the collision cross section for $J = 0$ to $J = 10$ is plotted in arbitrary units for an incoming velocity of $\nu = 1.14 \, \nu_t$, where ν_t is the threshold velocity for such inelastic processes. For $J \geq 4$, the total inelastic cross sections scale with the multiplicity of the state, which implies that the probability for inelastic scattering (with $\Delta J = 0$) is independent of J for the higher rotational states. This feature is unaffected by increasing the initial velocity. In addition, by $\nu = 1.8 \, \nu_t$, the $J = 2$ state grows until it scales with its multiplicity, and for very high velocities ($\nu = 4\nu_t$) the ground rotational states also do the same. In addition, this feature is further reinforced by the fact that, at a distance from threshold,
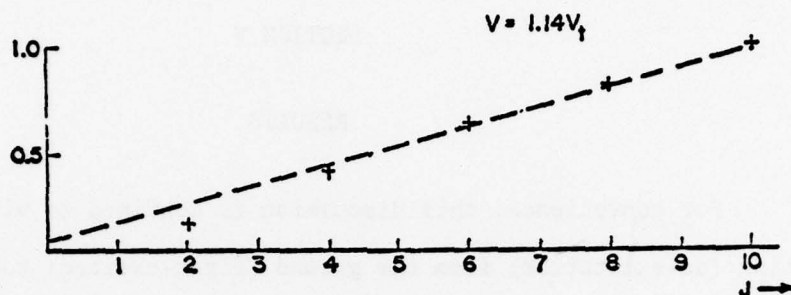
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Figure 1. Plot of normalized calculated cross
sections (in arbitrary units) as a
function of J.

$$\sigma_{J \to J'}/\sigma_{J' \to J} = 1 \pm 0.05 \qquad (7)$$

for all states through $J = 12$. In equation (7), $\sigma_{J \to J'},(\sigma_{J' \to J})$ is the

total inelastic scattering cross section for processes in which $\Delta \nu = 1$

and the rotational quantum number changes by means of $J \to J'(J' \to J)$.

(The small deviation from unity is due to small changes in the available

phase space for collision.)

Next, the importance of angular momentum in a vibrational-roational-

translational (V→R→T) collision is examined. Processes in which $\Delta J \neq 0$

represent additional channels through which the vibrational mode can

be excited or de-excited and as a result may play an important role

in gas kinetics. This will occur if the cross sections for $\Delta J \neq 0$

processes are of the same order of magnitude as the $\Delta J = 0$ channel. In

Figure 2 the quantities

$$R_{1,2 \to 0,J}(\nu) \equiv \frac{\sigma_{1,2 \to 0,J}(\nu)}{\sum_{j=0}^{18} \sigma_{1,2 \to 0,J}(\nu)} \qquad (8)$$
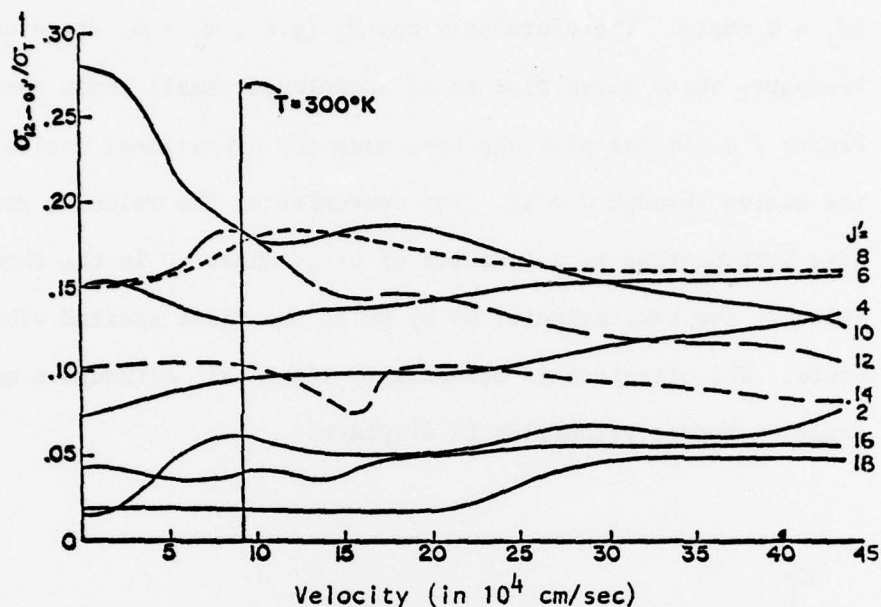
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Figure 2. Plot of normalized calculated cross sections
(in arbitrary units) for de-excitation of N_2
by He as a function of velocity.

are plotted for de-excitation of N_2 by He as a function of ν, the
incident velocity. Note that large quantities of angular momentum
are readily transferred. In particular, $\Delta J = 0$ processes amount to
less than 10% of the possible processes for thermal velocities of 1200°K
or greater. In addition, for thermal velocities of 300°K, processes
with $\Delta J = 12$ are of greater importance than those in which $\Delta J = 0$.
Furthermore, for a cold gas (105°K), processes with $\Delta J = 14$ are as
significant as those with $\Delta J = 0$. Thus, angular momentum transfer plays
an extremely important role in vibrational excitation. Note that,
except for the $J = 2 \rightarrow J = 0$ processes, these effects are not due to
multiplicity of the final state but arise from the selection rule

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$\Delta M_J = 0$ state. Therefore only one M_J (i.e., $M_J = 0$) state can par-
ticipate, which gives rise to an anomalously small cross section. In
Figure 3 a similar plot has been made for vibrational excitation includ-
ing states through $J = 12$. For convenience, the relative cross sections
have been plotted as a function of v/v_t, where v_t is the threshold
velocity for excitation of N_2 by He to the first excited vibrational
state. The situation is essentially identical, although a much greater
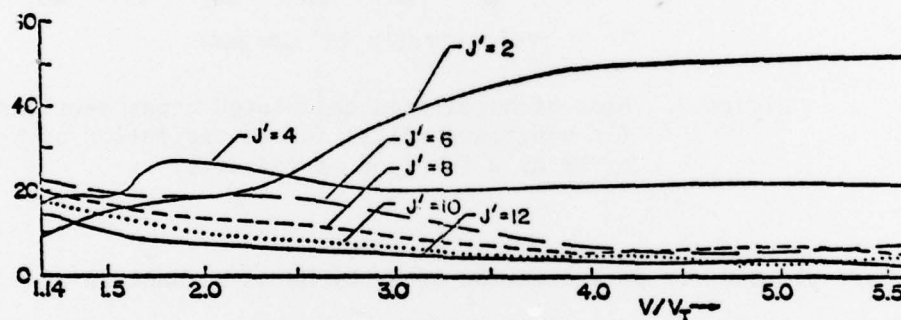range of impact velocities is displayed.

Figure 3. Plot of normalized calculated cross sections
(in arbitrary units) for excitation of N_2 by
He as a function of velocity.

An examination of Figure 3 reveals that as the incident velocity increases,
the $\Delta J = 0$ channel tends to dominate and the probability of creating
large quantities of angular momentum tends to decrease. However, even
at an incident velocity of $4v_t$, the $\Delta J = 0$ channel accounts for only
half the possible processes, so V→R→T processes are always of importance.
These features, i.e., large ΔJ, are quantum mechanical effects, which

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would not appear in semiclassical theories. This can be seen from the following semiclassical argument. The torque $\vec{\Gamma}$ exerted on the N_2 molecule is

$$\vec{\Gamma} = \frac{d\vec{J}}{dt} = \vec{r} \times \vec{F} \tag{9}$$

where $\vec{r}$ is the impact parameter and must lie within the range a of the force. The change in the rotational motion is approximately $\frac{a}{\overline{r}}$ torque, i.e.,

$$\delta J \simeq Fa^2/\overline{r} \tag{10}$$

In equation (7), $\overline{v}$ is the average of the initial and final velocities. Thus, on the basis of semiclassical considerations one expects that ΔJ should be small and that the cross sections $\sigma_{J \to J'}$, with $J \neq J'$ should fall off rapidly with increasing velocity. These features tend to appear only at high incident velocities ($v \sim 4v_t$), but note that even at $v = 5.5\ v_t$ quantum effects still remain.

Finally, the effect of molecular orientation on V→T processes is examined. For large values of J, the angular momentum behaves like a classical variable (with regard to the orientation of the molecule) and one can make a correspondence between the M_J state and a classical angle $\theta \equiv \cos^{-1}(M_J/J)$, which specifies the orientation of the molecule. Now, for situations in which the incident velocity is slightly greater than the threshold velocity, the momentum transfer vector is nearly parallel to the initial wave vector, i.e., the incident velocity. Since the momentum transfer vector defines the axis of quantization,

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it follows that states with $M_J = 0$ correspond to head-on or collinear

collisions (see inset in Fig. 4), whereas states in which $M_J = \pm J$

correspond to the case in which the N_2 molecule is normal to the incident

velocity. In Figure 4, the inelastic collision cross section is plotted

in arbitrary units for the V→T process with $J = 12$ and $\Delta v = 1$, as a

function of M_J (or θ). The large central peak corresponds to the fact

that head-on collisions tend to dominate V→T rates. Furthermore, the

configuration in which the molecule is normal to the incident velocity

(i.e., $M_J = \pm J$) does not participate in the collision. These features

are expected within a classical model. However, the cross section does

not fall off smoothly as $\left|M_J\right|$ varies from zero to J, but instead dis-

plays considerable structure with intermediate peaks. Again, these

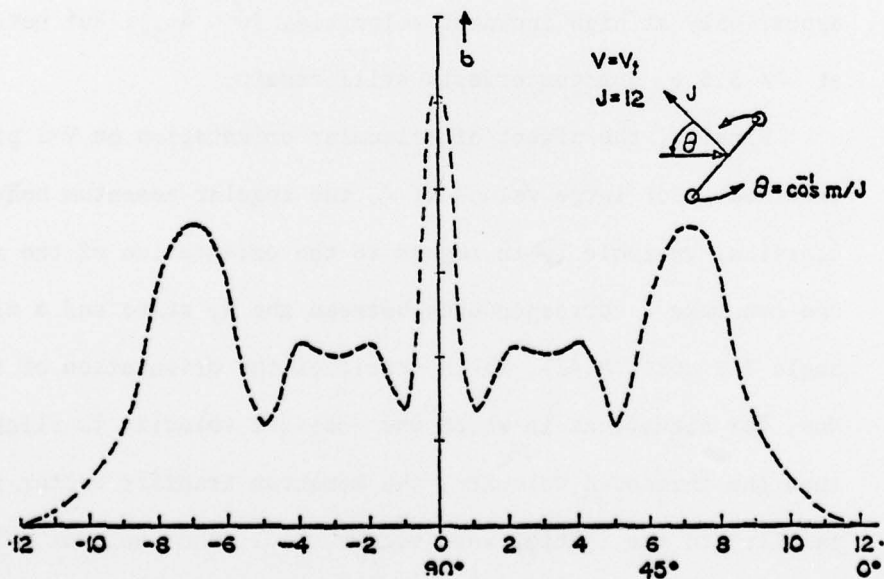features arise from quantum effects.

Figure 4. Plot of normalized calculated cross sections
(in arbitrary units) as a function of the M
quantum number.

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In conclusion, changes in the molecular rotation are of significant importance in vibration collision processes and dominate deactivation processes at thermal velocities.

SECTION VI

FIFTH WINTER COLLOQUIUM

As required by the Statement of Work, the Fifth Winter Conference
on Quantum Electronics was held from February 1-6, 1975, at Snowmass,
Colorado. The emphasis was on electronic transitions, chemical and
collisional pumping of electron transitions, and short wavelength
optics. Particular emphasis was paid to molecular physics, E-collision
pumping, excitation mechanics, short wavelength lasers, and short
wavelength resonators.

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